Enhancing Oxygen Stability In Low-Cobalt Layered Oxide Cathode Materials

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Project ID: bat414

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Overview

Timeline

- Project start date: 12/01/2018
- Project end date: 12/31/2021
- Percent complete: 40%

Barriers

- Barriers addressed
  - Cost
  - Performance
  - Life

Budget

- Total project funding $3.125 million
  - DOE Share $2.5 million
  - Contractor share $625K
- Funding for FY 2019: $1.15 million
- Funding for FY 2020: $1.01 million

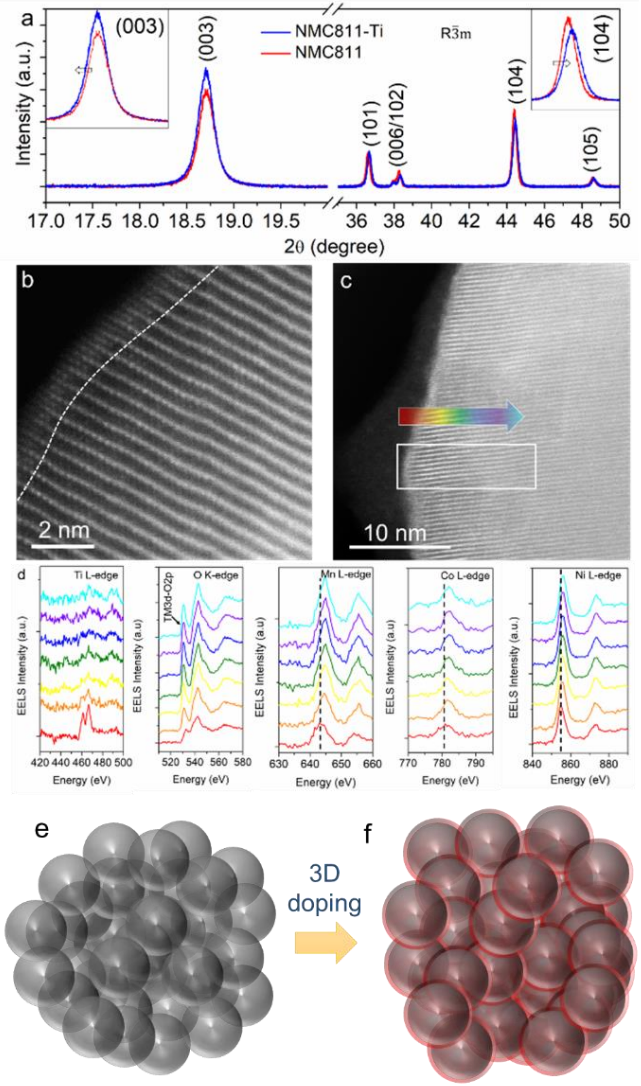
Partners

- UC Irvine: Project Lead Huolin Xin
- Virginia Tech: Feng Lin
- UC Berkeley: Kristin Persson
- PNNL: Wu Xu
- American Lithium Energy: Jiang Fan
- Collaborations: BNL, NSLSII, SSRL

Relevance: Objectives

Overall objectives

- Displace Co while maintaining high-Ni content and high energy density
  - Cobalt concentration < 50 mg/Wh or No-Co
  - Energy density > 750 Wh/kg (C/3, 2.5-4.4 V) at cathode level
  - Cost ≤ $100/kWh
- Improve cycle and calendar life by retaining oxygen through a 3D doping technology
  - Capacity retention > 80% at 1,000 cycles
  - Energy retention > 80% at 1,000 cycles
  - Calendar life: 15 years
- Deliver a theoretical model
  - High-throughput DFT calculations that rationalize the selection of oxygen-retraining surface and bulk dopants
- Formulate new electrolytes
  - New functional additives
  - Understanding of the CEI's influence on high-Ni low-Co cathodes.
- Offer a knowledge base by performing proactive studies
  - Thermal stability, oxygen loss, and the degradation of the cathode/electrolyte interfaces.



Milestones

Milestone	Status	Description
Jan 2019 Dopant Selection and Material Synthesis	Completed	Computational down-selection to 2–4 elements for synthesis. Achieve NMC-D electrode materials with Co content <= 3%, Ni >= 90%, Dopant metal (Ti or Al) = 2%
April 2019 Structural Fidelity	Completed	Structural study by synchrotron XRD, and aberration-corrected scanning TEM to confirm that the desired layered structure and 3D composition are achieved.
July 2019 Electrode Performance and Fabrication of PPCs	Completed	Evaluate electrochemical performance of BP 1 materials and compare it with the commercial 811 baseline >100 cycles in Li||NMC cells at 4.5 V cutoff and Gr||NMC cells at 4.4 V cutoff. Delivery of PPCs to DOE.
October 2019 Go/No Go	Completed	Delivery of a high-Ni and low-Co cathode material with an electrochemical performance comparable to the commercial NMC811 baseline (energy and capacity retention > 90% of NMC811 @ 100 cycles).

Milestone	Status	Description
Jan 2020 Dopant Refinement	Completed	Refine prediction of surface/bulk dopants
April 2020 Synthesis Scale-up	On track	Scale up synthesis of BP 1 materials to 100 g scale.
July 2020 Performance Evaluation	On track	Best of BP1 and BP2 materials achieves a comparable performance to the 811 baseline >300 cycles in Gr||NMC pouch cells at 4.4 V cutoff.
Oct 2020 Go/No Go	On track	Delivery of a high-Ni and low-Co cathode that has a comparable performance to the NMC811 baseline. (Energy target = 650-750 Wh/kg C/3, 2.5-4.4 V at the cathode level; capacity retention: 70%-90% at 500 cycles; cobalt concentration: 50 mg - 70 mg/Wh)

Approach/Strategy

- **We utilize a three-dimensional (3D) doping technology that is a hierarchical combination of surface and bulk doping.**
  - Surface doping stabilizes the interface between the primary particles and the electrolyte
  - Introduction of dopants to the bulk enhances oxygen stability, conductivity and structural stability in low-Co oxides under high voltage and deep discharging operating conditions.
  - A composition controlled and thermodynamics driven synthesis will be used to accurately achieve the desired 3D doping structures.
- **Use high-throughput computational materials design to screen surface and bulk dopants for a low-Co environment.**
- **Formulate new electrolytes that stabilize the cathode/electrolyte interfaces at deep charging conditions.**
- **Advanced computational and characterization techniques are developed to study**
  - Dopant environment and chemistry
  - Thermal stability, oxygen loss, and the degradation of the cathode/electrolyte interfaces.

Technical Accomplishments and Progress
Gen-1 Material: 2% Ti-doped NMC-811

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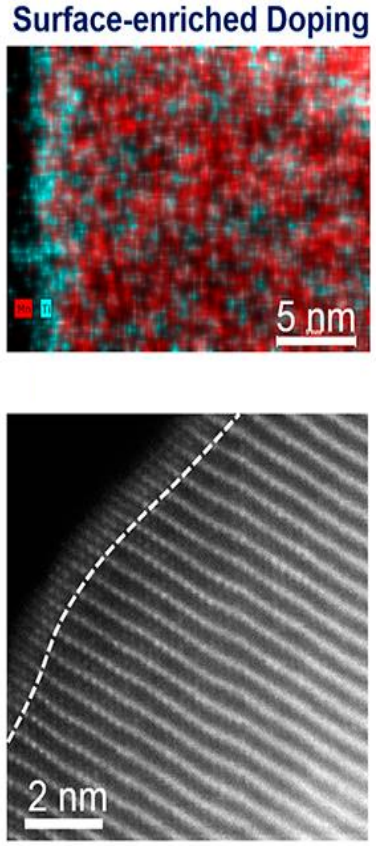
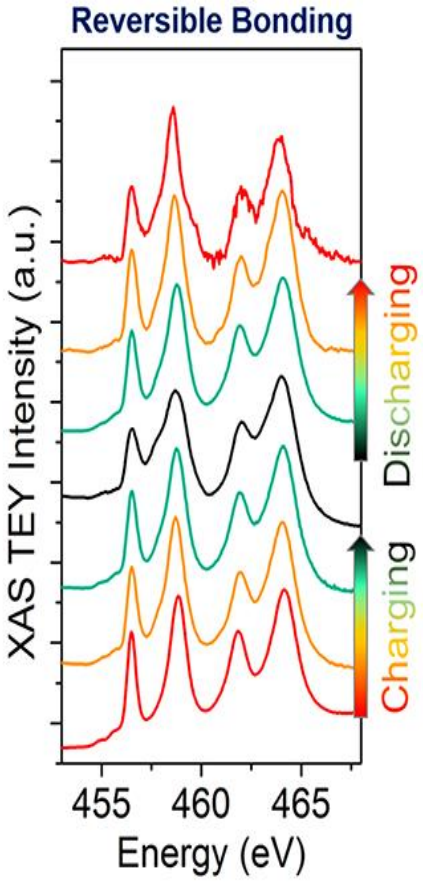
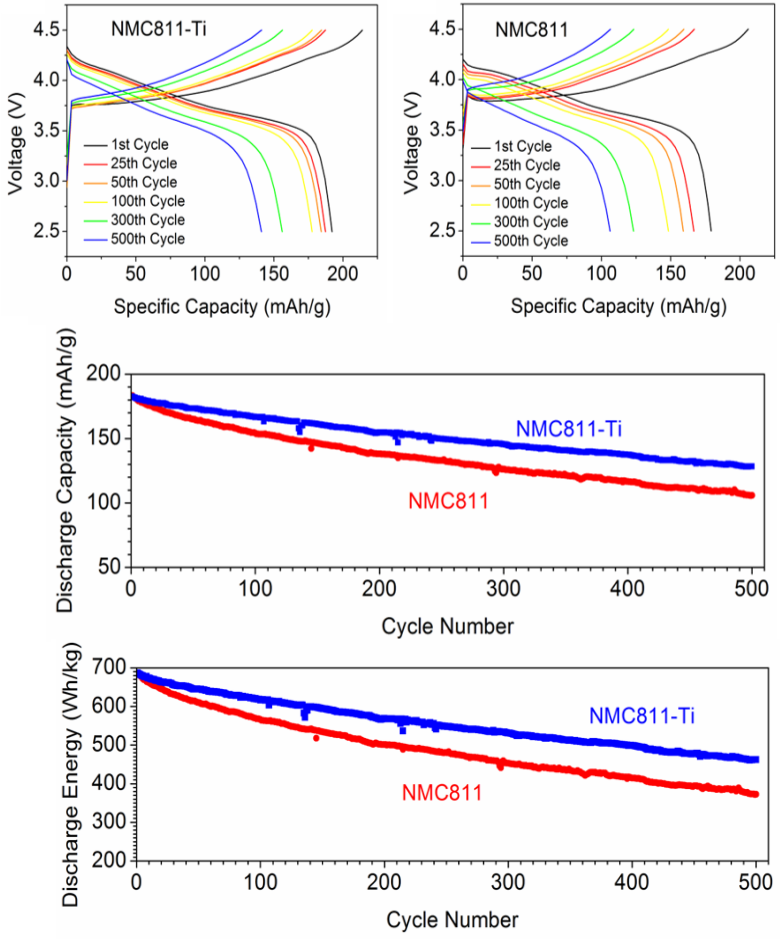
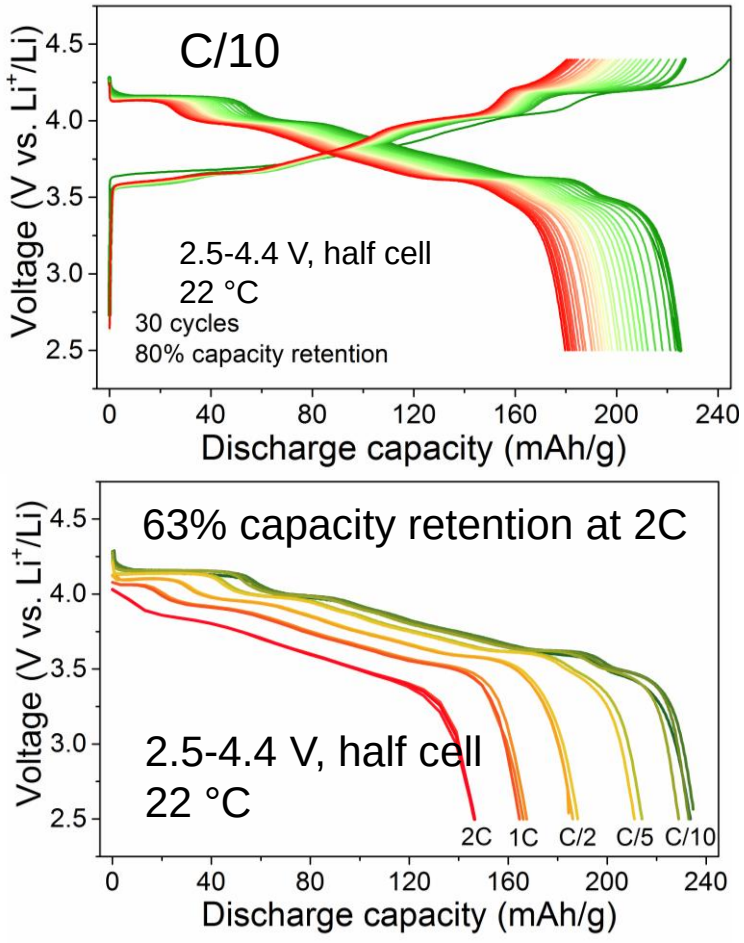






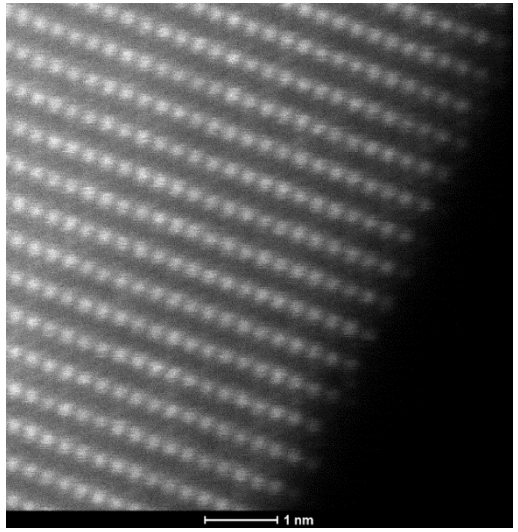
$LiNiO_2$

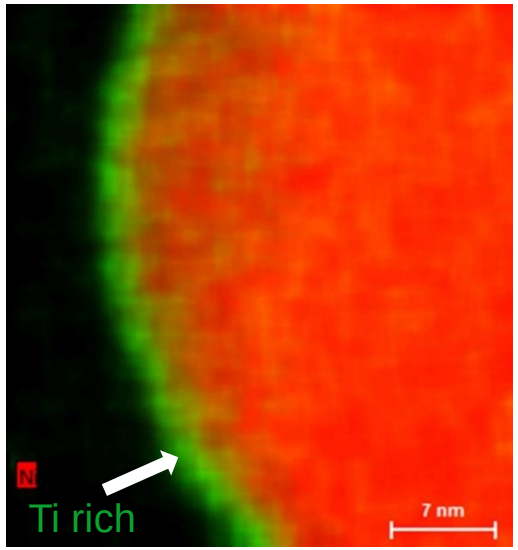


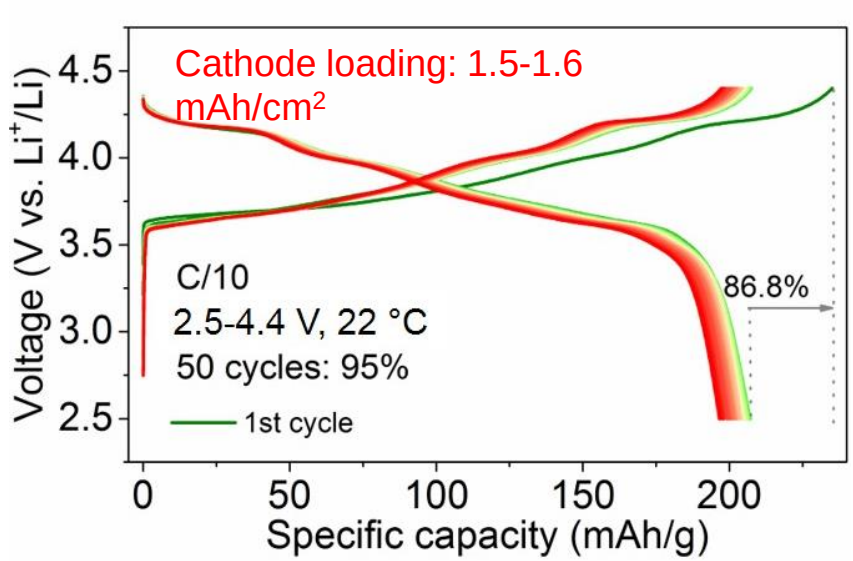
- **3D-doping of Ti is achieved in NMC-811 and cycle life is significantly improved.**
- **Can we use the 3D doping approach to improve $LiNiO_2$?**

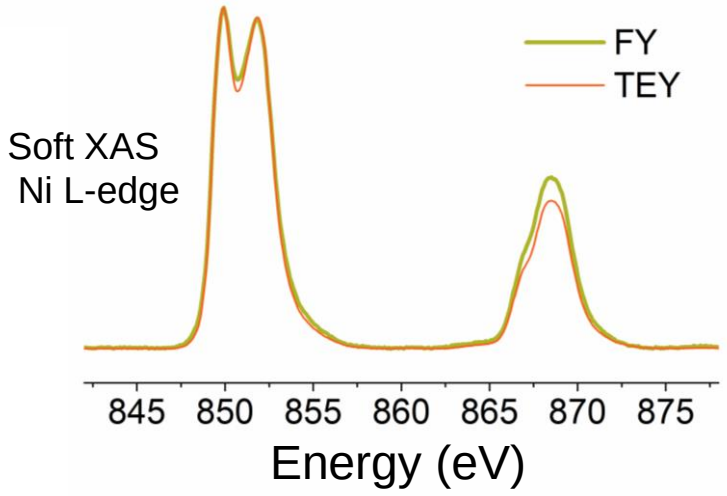
ACS applied materials & interfaces 11 (41), 37885-37891

Technical Accomplishments and Progress
Gen-2 Co-free Chemistry: 3D-doped $LiNiO_2$ [Ni 96%, Mg 2% , Ti 2%]

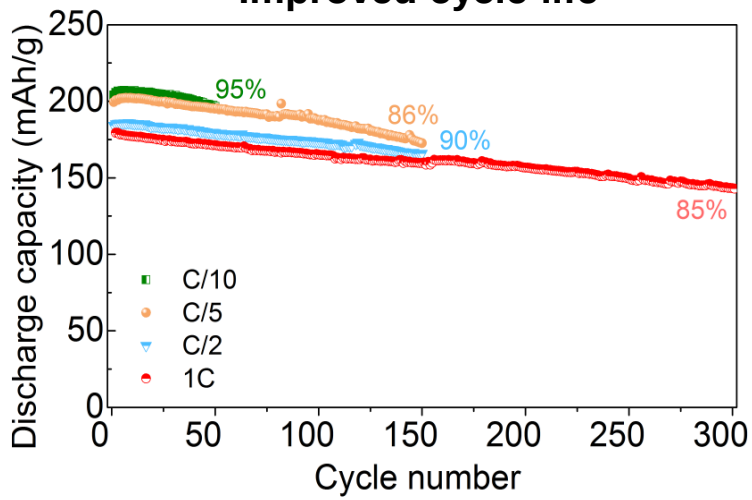




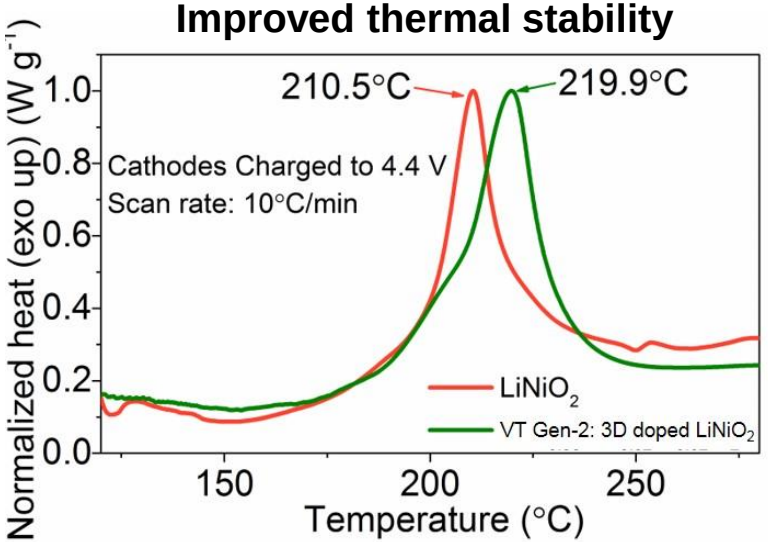




Improved cycle life



Improved thermal stability



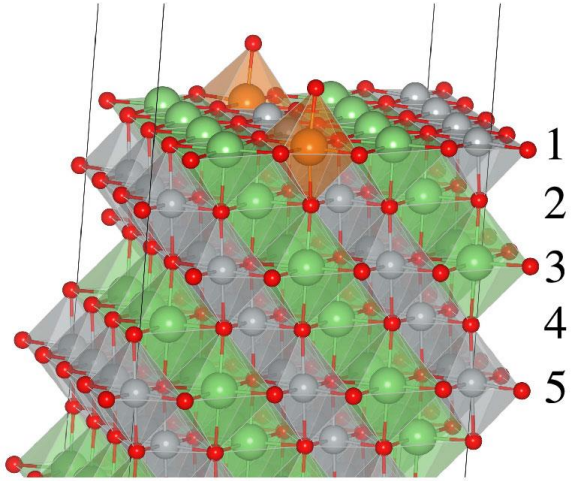
- **3D-doping of Ti and Mg is achieved in $LiNiO_2$. Cycle life and thermal stability are much improved compared with $LiNiO_2$.**

Chemistry of Materials 31 (23), 9769-9776

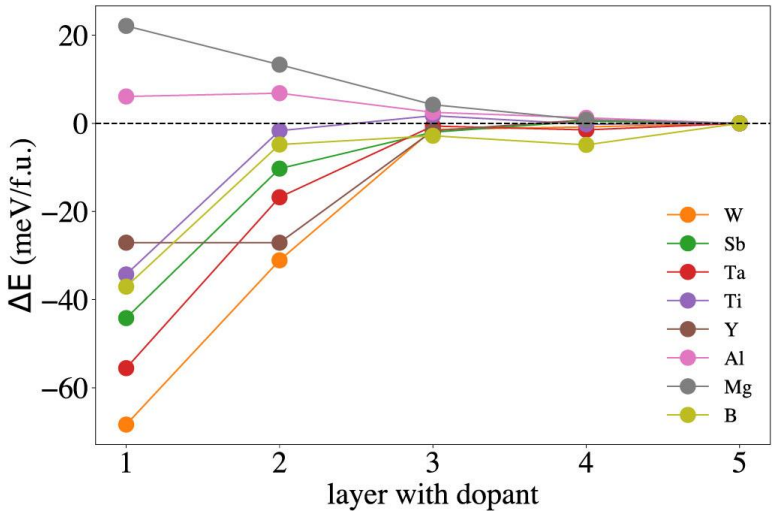
Technical Accomplishments and Progress
Rationalize Surface Dopant Segregation

Dopant Segregation Energy

$LiM_{0.019}Ni_{0.981}O_2$ (104)



$\Delta E = E_{il} - E_{5l}$



Total number of atoms: 217 (53 Ni + 1M)

$\Delta G = \Delta H - T\Delta S = \Delta H + TNk_B(x_A lnx_A + x_B lnx_B) = 0$

Take $\Delta H = \Delta E = \mathbf{20\ meV/f.u.}$, $\boldsymbol{T = 2517\ K}$

For Al, $\Delta H = \Delta E = \mathbf{6\ meV/f.u.}$, $\boldsymbol{T = 755\ K}$

$LiNiO_2$ is synthesized around **900 K**

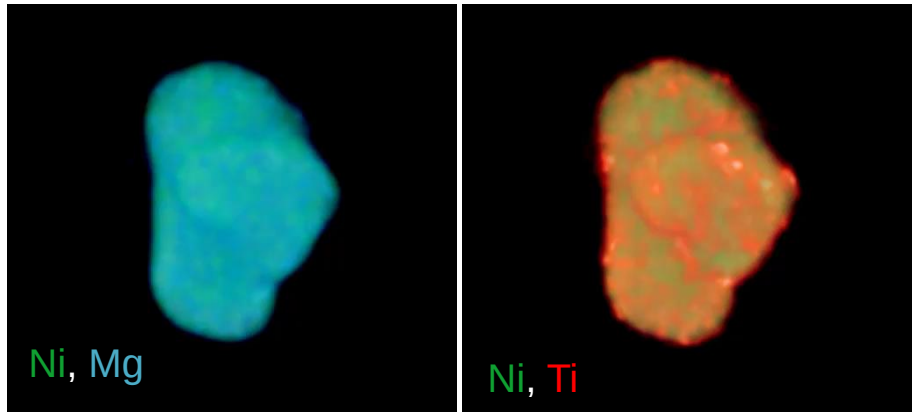
Bulk-enrich: **Mg**

Surface enrich: **W, Sb, Ta, Ti, Y, B**

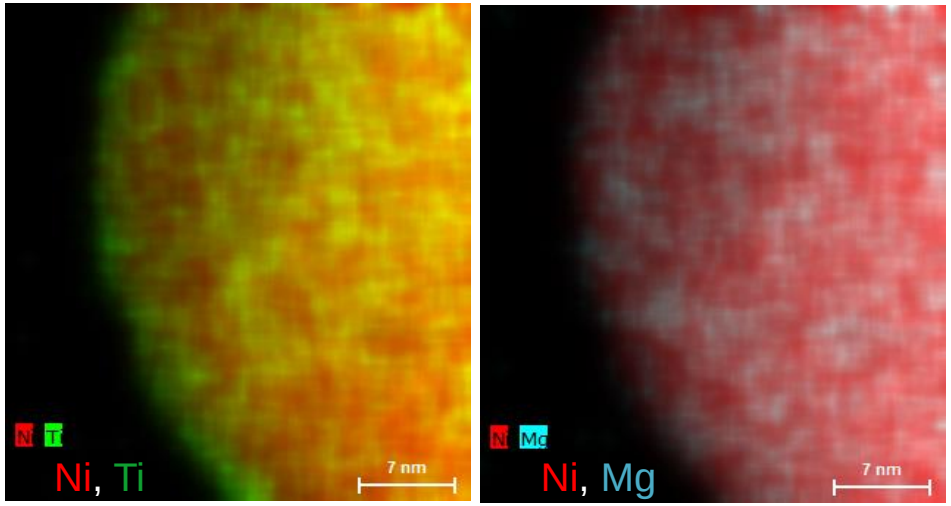
Uniform: **Al**

- **Dopant segregation behavior is thermodynamically driven**

Chemical Electron Tomography

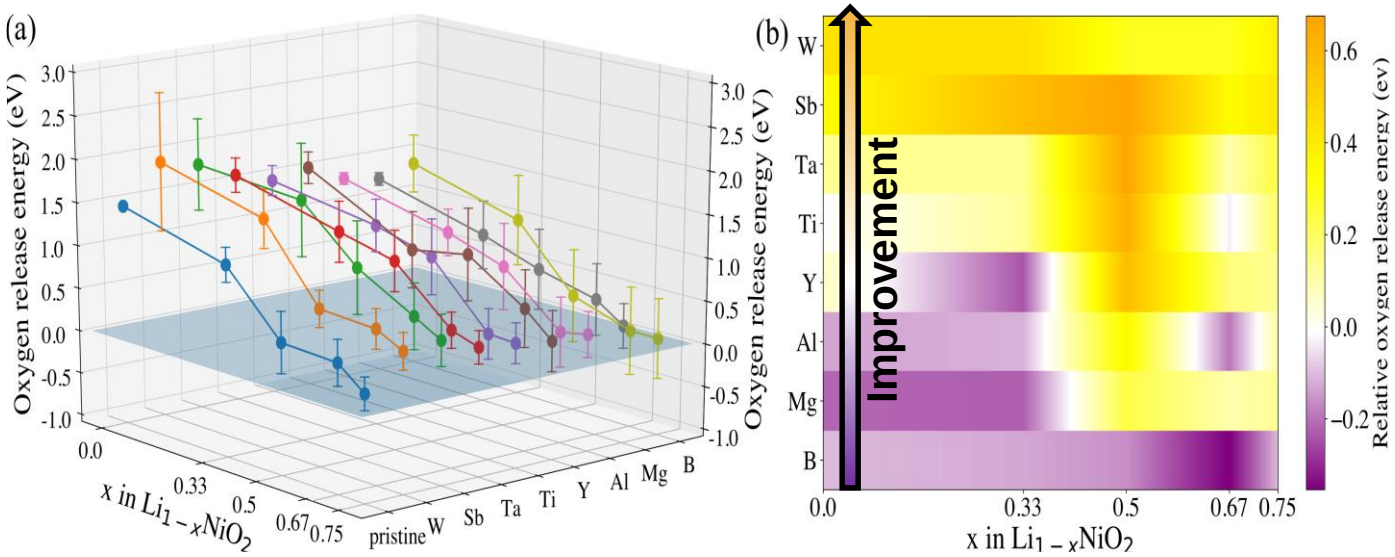


Concentration Map



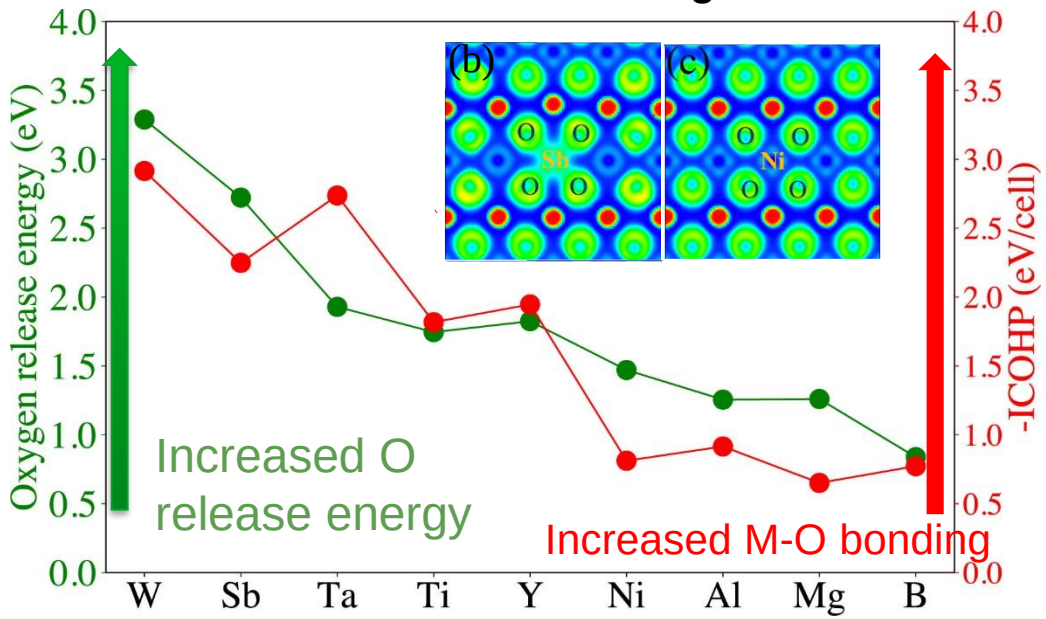
Technical Accomplishments and Progress
Computational Downselection of Oxygen Retaining Surface Dopants

Oxygen Release Energy



- Upon delithiation, the thermodynamic oxygen release energy decreases rapidly
- At high charge state, e.g. 75% of Li extraction, oxygen is close to spontaneously release from the surface for pristine LNO

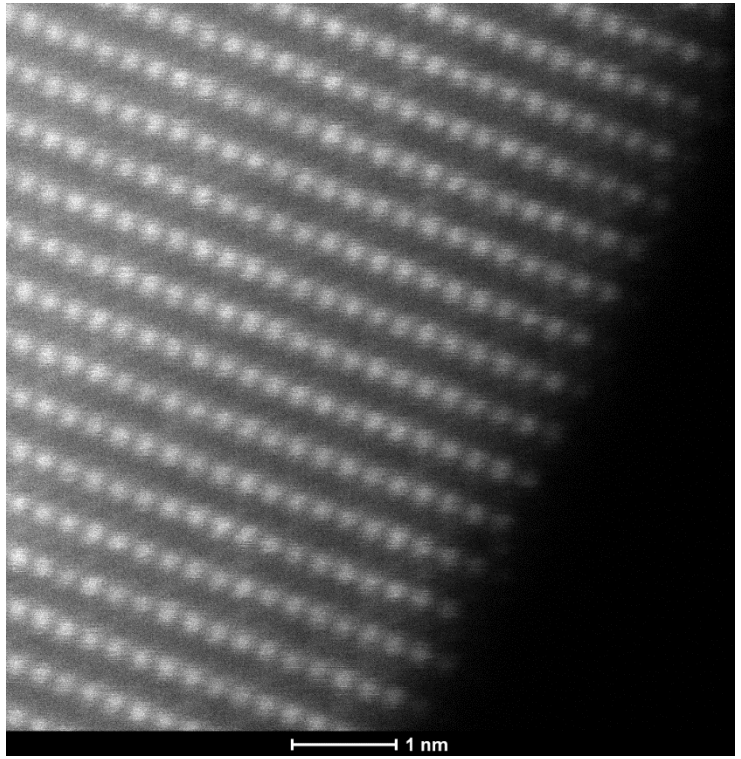
M-O Bond Strength

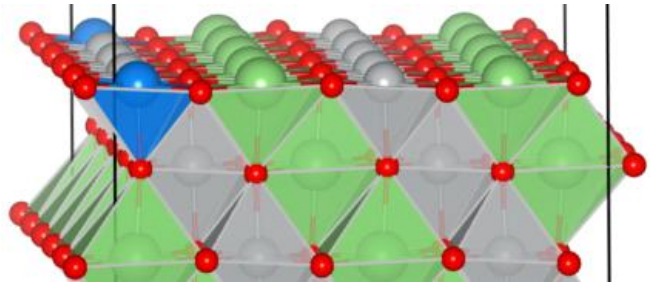


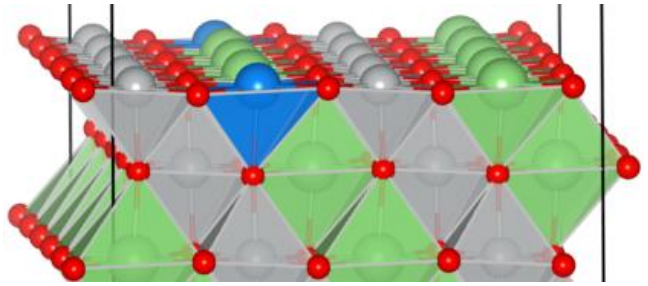
- W, Sb, Ta, and Ti bond more strongly to oxygen than Ni, Al, Mg, and B, and reduce the oxygen release.

- **W, Sb, Ta and Ti** are found to enhance **surface** oxygen retention of $LiNiO_2$

Technical Accomplishments and Progress
Preferential Site on the Surface



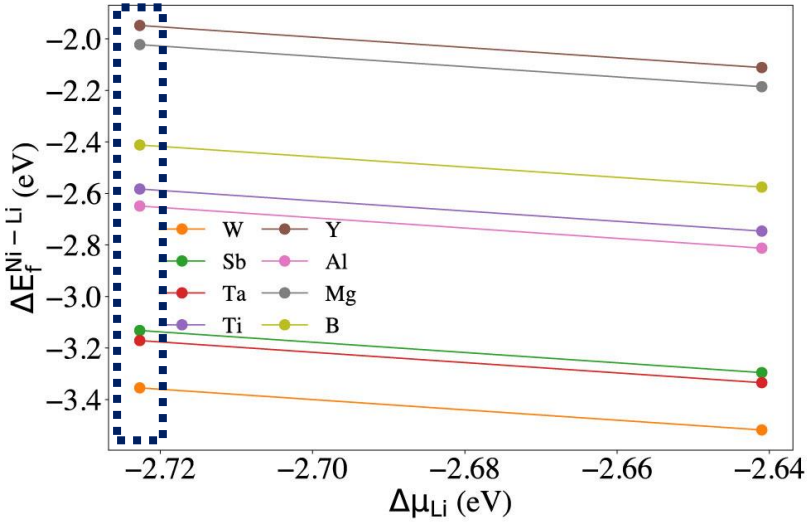


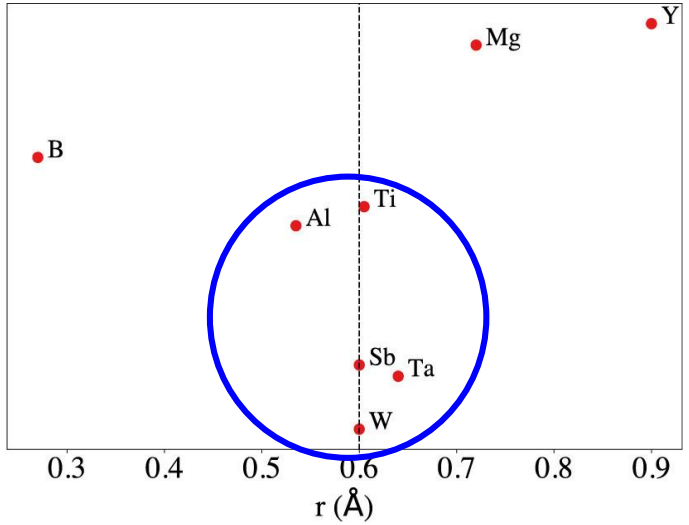


Green: Li Grey: Ni Red: O Blue: Dopant

ΔE_f^{Ni-Li}: Formation energy difference between doping at Ni and Li site

A negative ΔE_f^{Ni-Li} implies Ni site is more favorable than Li site.

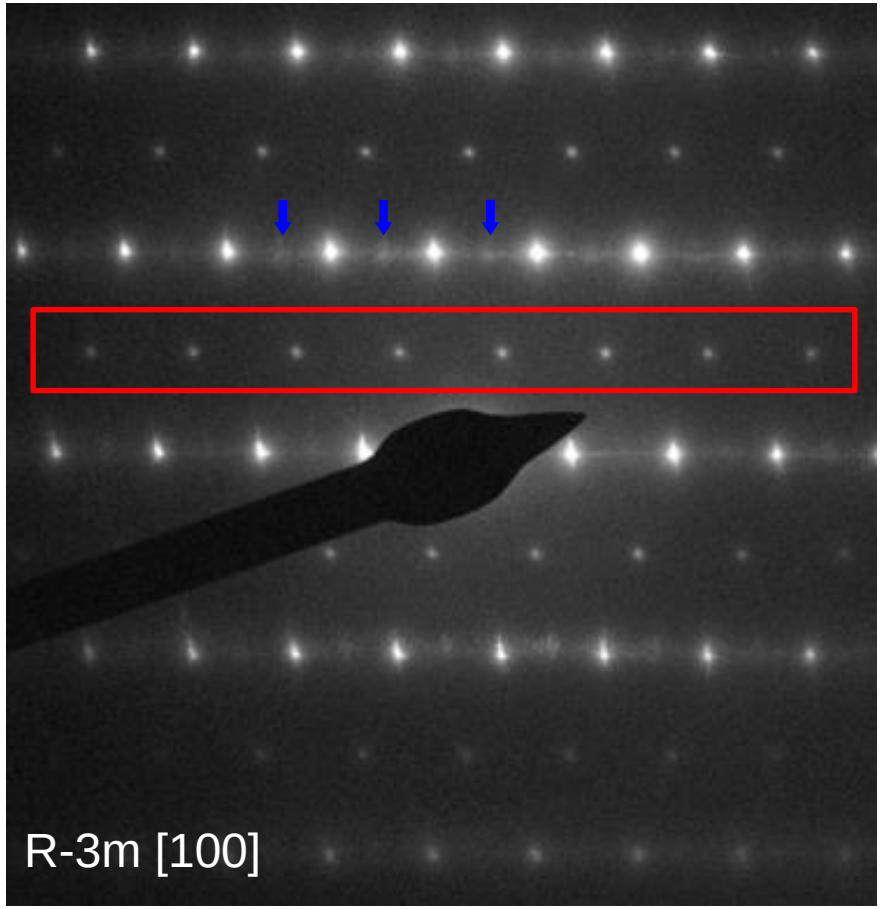




- **Ti, Al, Sb, Ta and W at low concentration tend to stay in the Ni site on the surface of $LiNiO_2$**

Technical Accomplishments and Progress
Structure of charged MgTi-doped $LiNiO_2$ vs $LiNiO_2$

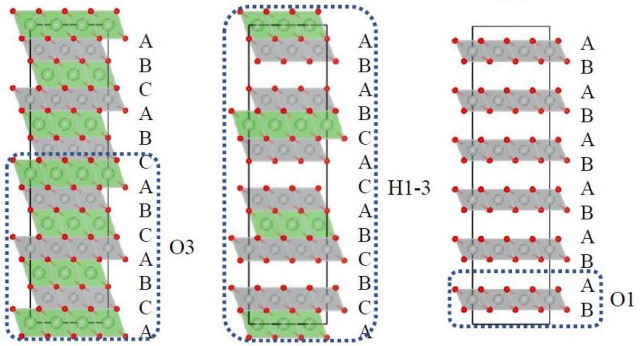
Delithiated LNO (at 4.4 V)



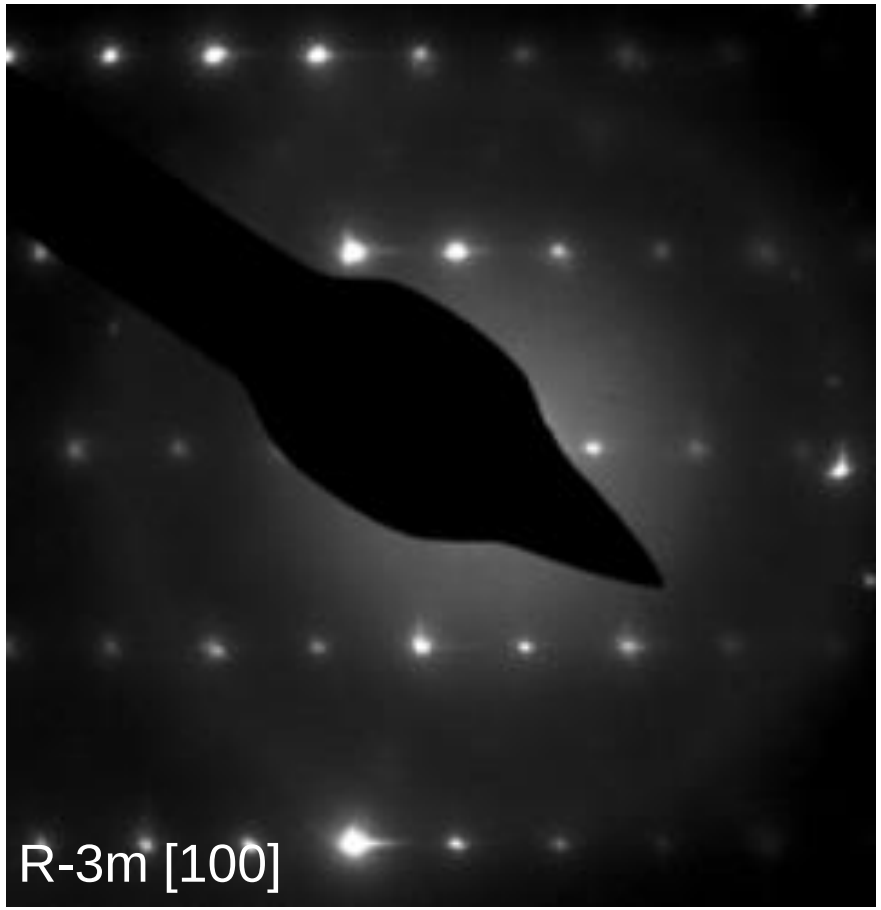
Extra spots: H1-3 phase

Cation mixing

Streaking: SFs

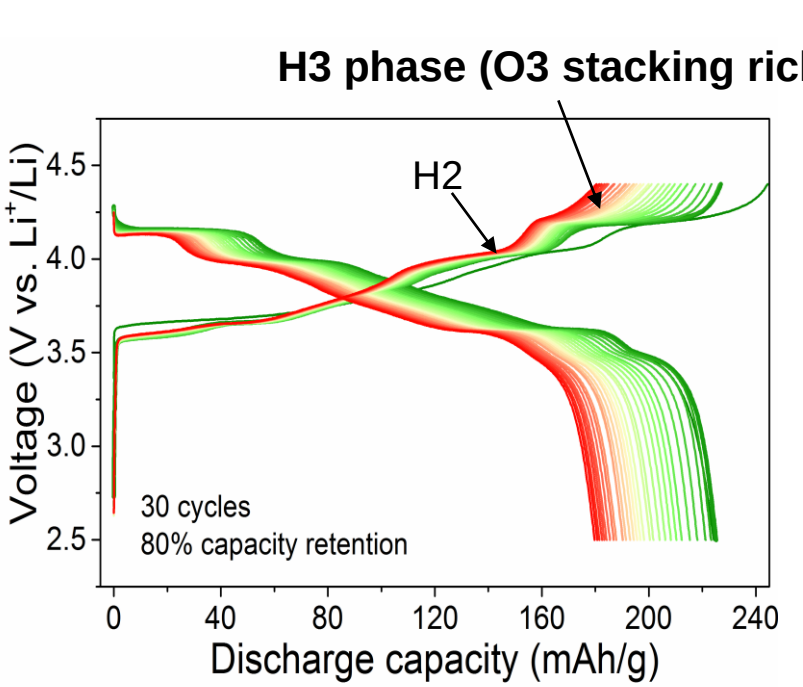


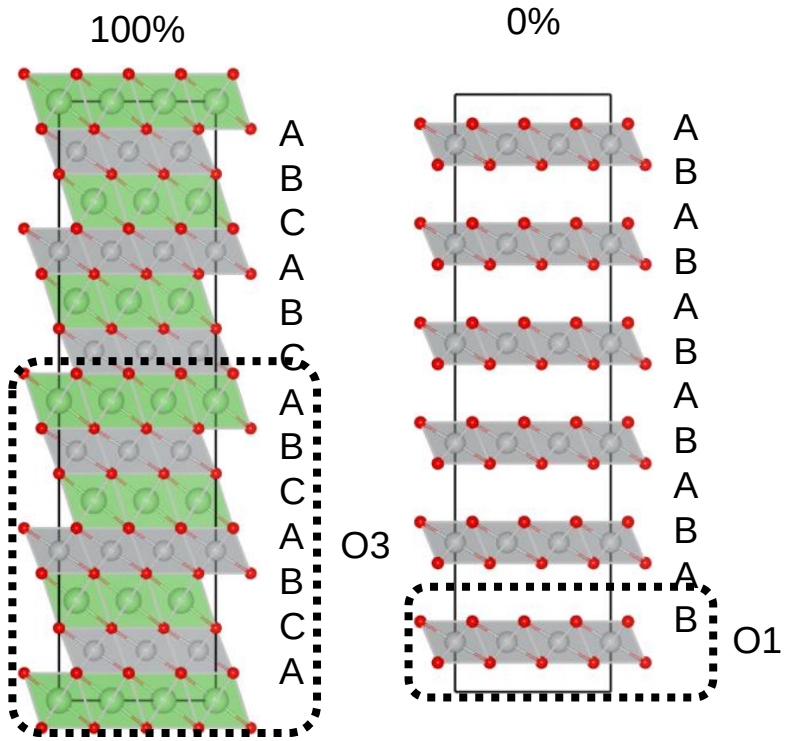
Delithiated MgTi-doped LNO (at 4.4V)

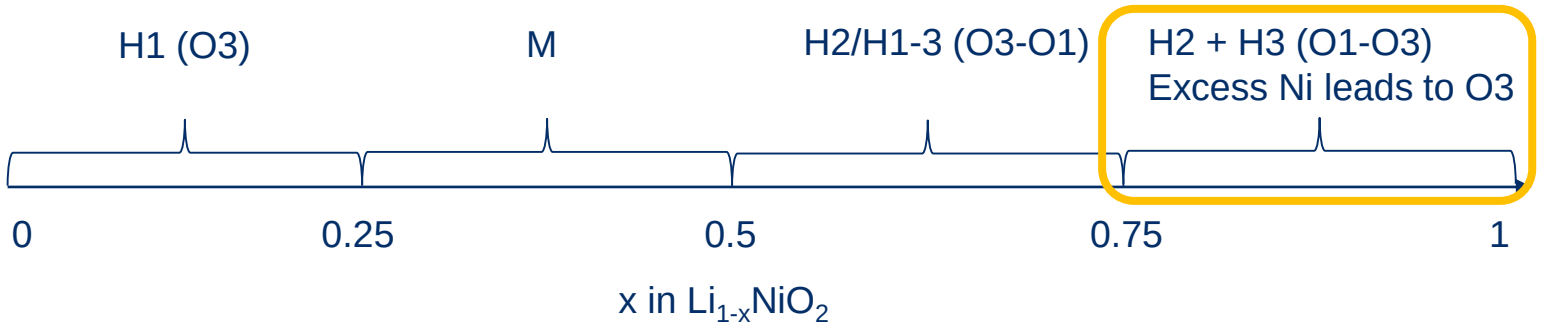


- **MgTi co-doping reduces the transition to H1-3 phase and reduced SFs. It also reduces cation mixing.**

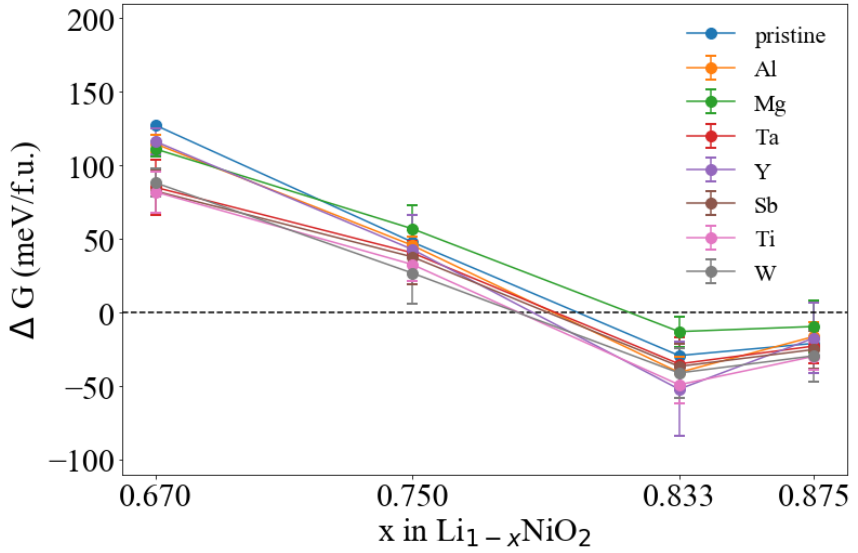
Technical Accomplishments and Progress
Reducing the Destructive Phase Transition







Free-energy calculation with doping concentration: 2.1%/2.8%



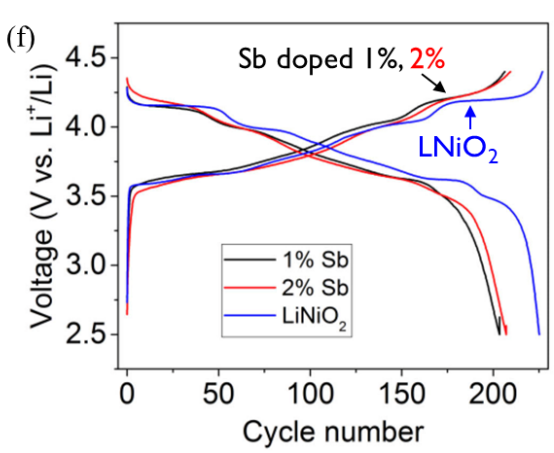
Pristine
- $\Delta G = 0$ at $x \approx 0.8$: H2+H3 two-phase region appears when $x > 0.8$

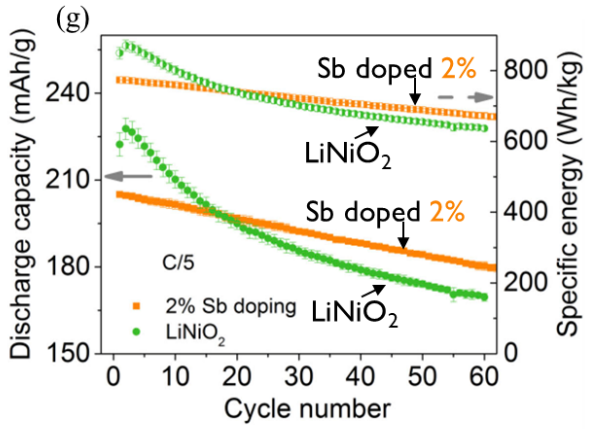
Doped-$LiNiO_2$
- Effective dopants: **Mg (2.1%~2.8%)**

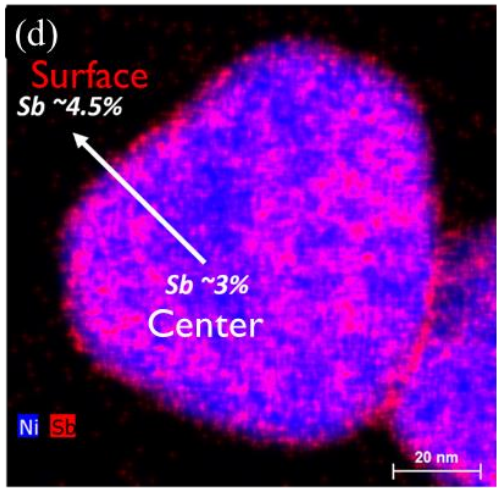
- **Mg is an effective dopant because it can inhibit the H2-H3 two-phase transition.**

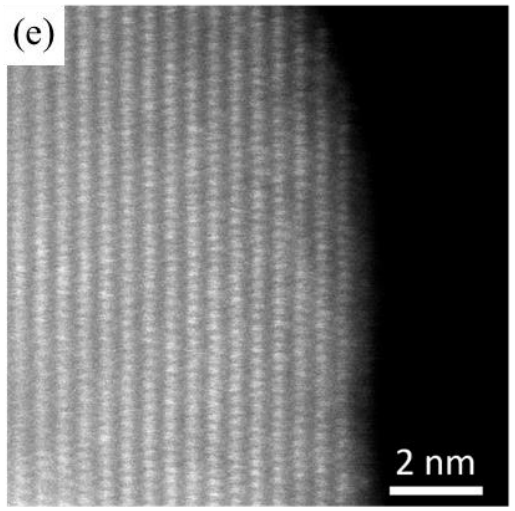
Technical Accomplishments and Progress
New Co-free Chemistries Under Investigation

$LiNiO_2$ with 2% Sb doping

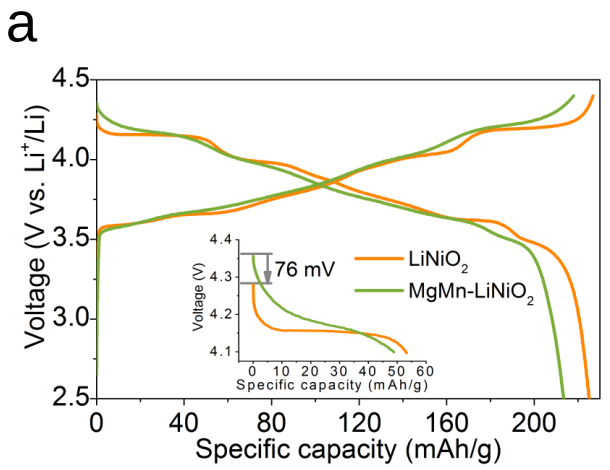


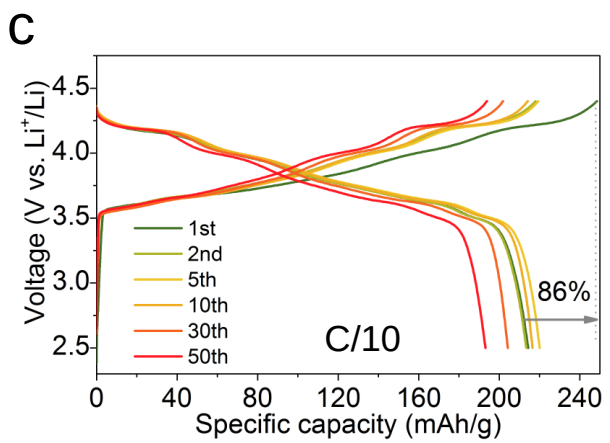


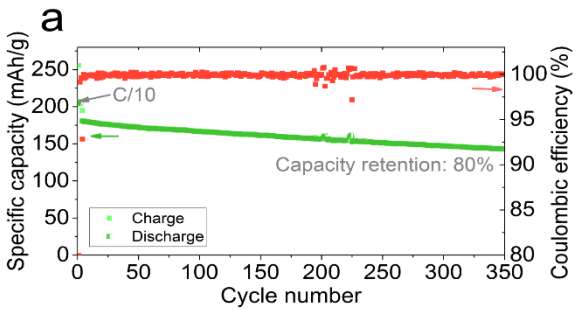


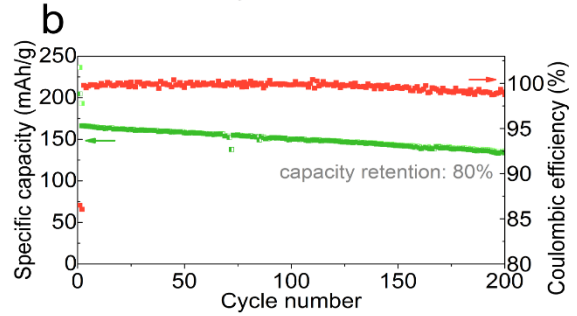


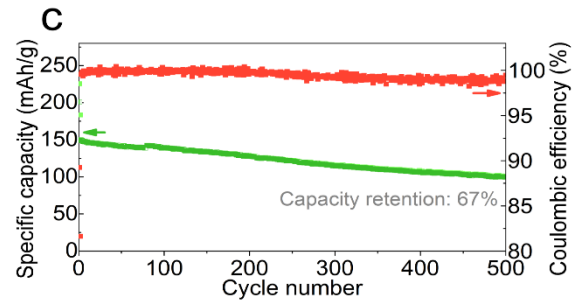
$LiNiO_2$ with 2% Mg, 2% Mn co-doping











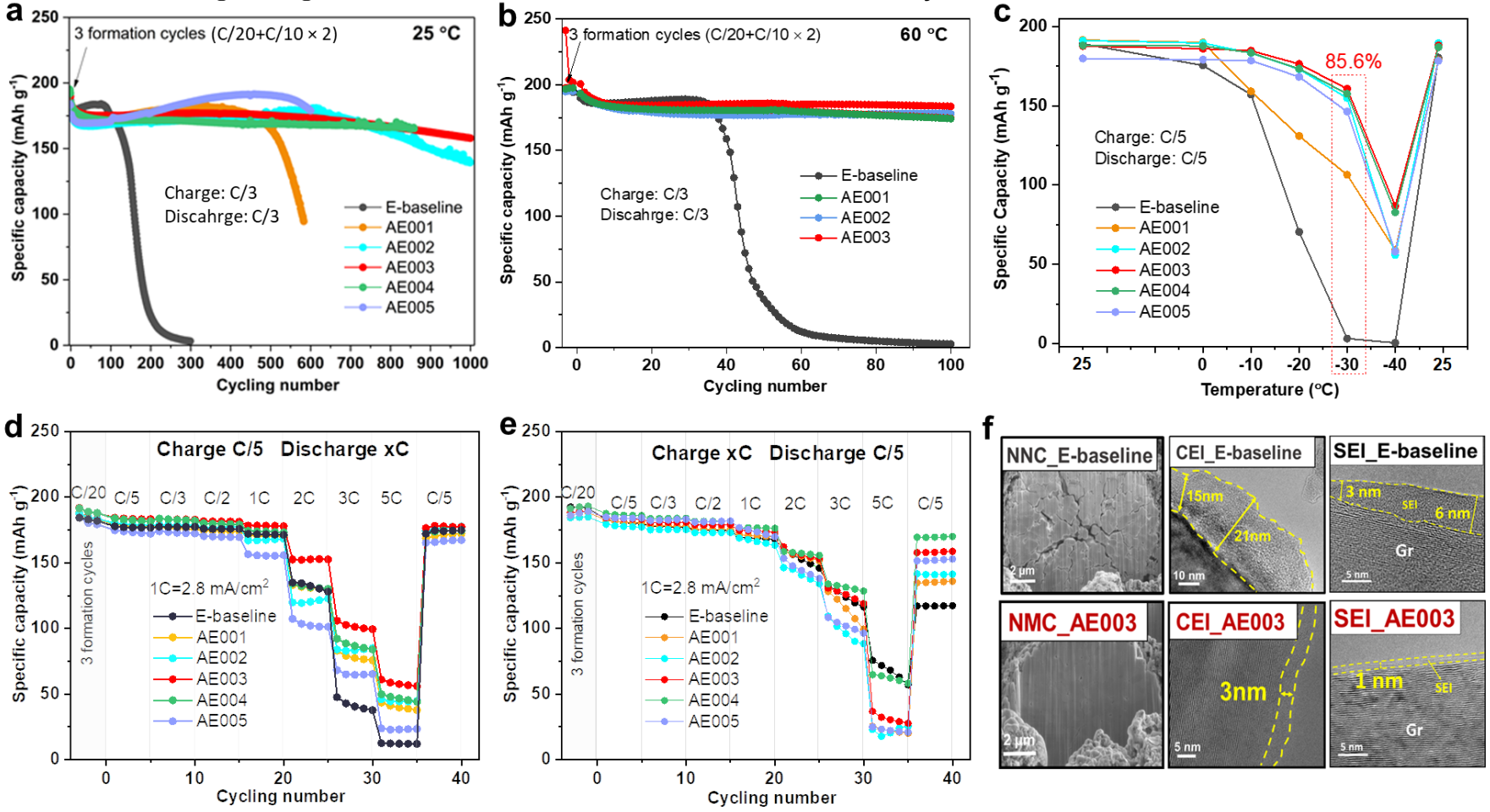
- **Two new Co-free chemistries have shown promising electrochemical performance.**

ACS Applied Materials & Interfaces 12 (11), 12874-12882

Technical Accomplishments and Progress
Development of DMC-based LHCEs for Gr||NMC811

- 5 new LHCEs (LiFSI in DMC-EC/VC-TTE) were developed for Gr||NMC811 cells.
- NMC811: 2.8 mAh cm^{-2}; Gr: 3.5 mAh cm^{-2} (Both from ALEC).
- Voltage range: 2.5 – 4.4 V, 1C= 2.8 mA cm^{-2}. 3 formation cycles: 1×C/20 + 2×C/10.

E-baseline
1.0 M LiPF6 in EC-EMC (3:7 by wt.) with 2 wt% VC



- ✓ AE003: Best cycling stability
  - 25°C: η(1000th)=85.8%
  - 60°C: η(100th)=94.9%
- ✓ AE003 & AE004: Better low-T discharge performance. For AE003:
  - -10°C: 98.5% of "25°C"
  - -30°C: 85.6% of "25°C"
- ✓ AE003 and AE004: Best rate capability during charging and discharging up to 3C.
- ✓ AE003: Effectively suppressed particle cracking.
- ✓ AE003: Resulted in ultrathin, uniform SEI/CEI compared to E-baseline.

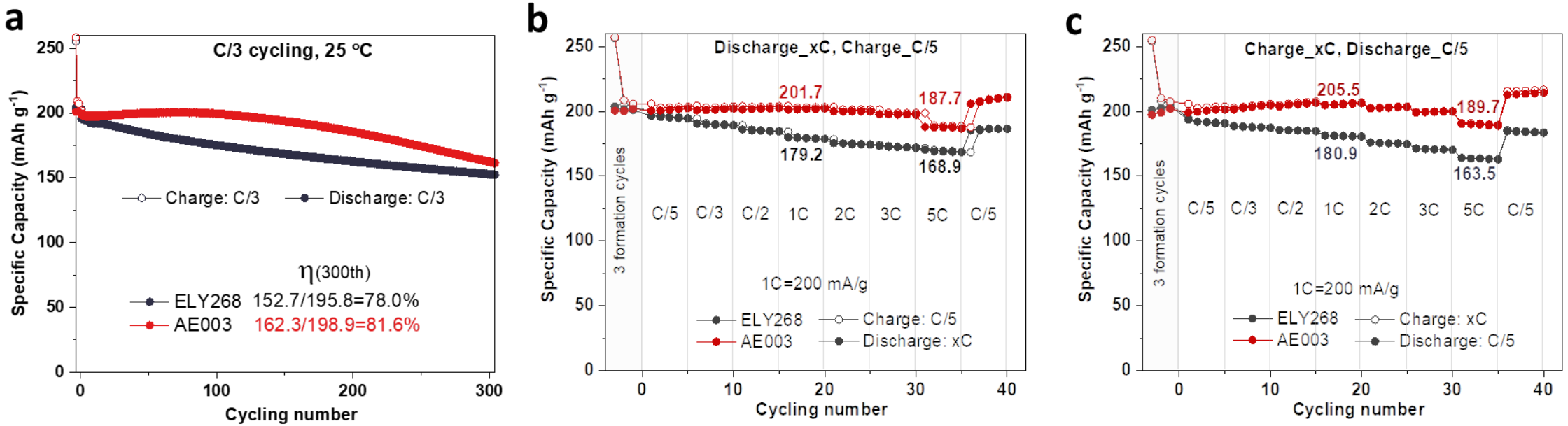
- **All LHCEs enable thinner, more uniform and robust SEI/CEI, showing much better cycling stability, rate capability and low-temperature discharge performance than E-baseline.**
- **AE003 shows the best electrochemical performances among the 5 LHCEs.**

Advanced Energy Materials, 2020,
DOI: 10.1002/aenm.202000368

Technical Accomplishments and Progress
New NMT from scaled-up precursor: Gr||NMT

- NMT was prepared from the scaled-up precursor (100g/batch).
- NMT: 1.5 mAh cm^{-2} (Coated at PNNL); Gr: 1.8 mAh cm^{-2} (From ANL CAMP)
- Voltage range 2.5 – 4.4 V, 1C = 1.5 mA cm^{-2} (200 mA g^{-1})
- 3 formation cycles: 1×C/20 + 2×C/10.

ELY268 (E-baseline)
1.0 M LiPF6 in EC-EMC (3:7 by wt.) with 2 wt% VC



- **New NMT material shows higher discharge capacity in AE003 than in ELY268 (i.e. E-baseline) during cycling and rate capability tests.**
- **AE003 enables superior cycling stability of Gr||NMT, with a capacity retention of 81.6% after 300 cycles.**
- **Gr||NMT cells with AE003 show superior discharge rate capability, with negligible capacity decay up to 3C, 187.7 mAh g^{-1} at 5C and 100% recovery after back to C/5.**
- **Gr||NMT cells with AE003 show better fast charging ability than with ELY268, with negligible capacity decay up to 3C, 189.7 mAh g^{-1} at 5C and 100% recovery after back to C/5.**

Responses to Previous Year Reviewers' Comments

- There are no reviewers' comments on this project.

Collaboration and Coordination with Other Institutions

Sub-recipients	Institution	Tasks
Feng Lin	Virginia Tech	Synthesis and X-ray Diagnostics
Kristin Persson	UC Berkeley	High-throughput DFT calculation
Wu Xu	PNNL	Synthesis scale-up and electrolyte formulation
Fan Jiang	American Lithium Energy	Electrode and Cell Fabrication

Collaborators	Institution	Nature of Collaboration
Xiao-Qing Yang	Brookhaven National Lab	X-ray Diagnostics
Kim Kisslinger	Brookhaven National Lab	FIB Sample Prep
Dennis Nordlund	SSRL/SLAC	Soft X-ray Absorption
Jack Kan	Australian Nuclear Science and Technology Organisation. Now at China Spallation Neutron Source.	Neutron Scattering Refinement

Remaining Challenges and Barriers

- Improving the thermal stability of these extremely high nickel content chemistries.
- Scale-up of calcination to the hundreds of grams per batch level for project completion cell delivery.

Proposed Future Research

- Deploy the developed electrolytes to single-layer and 2Ahr-scale pouch cells.
- Investigation of cathode-anode cross-talk and study the cathode electrolyte interface and interphases.
- Develop calcination conditions for scaled up synthesis.
- Develop new Co-free chemistries with thermal stability comparable to NMC-622.
- Use experimentally observed surface and bulk transformation and degradation pathways to refine the selection of surface/bulk stabilizing elements for Co-free materials.

Any proposed future work is subject to change based on funding levels

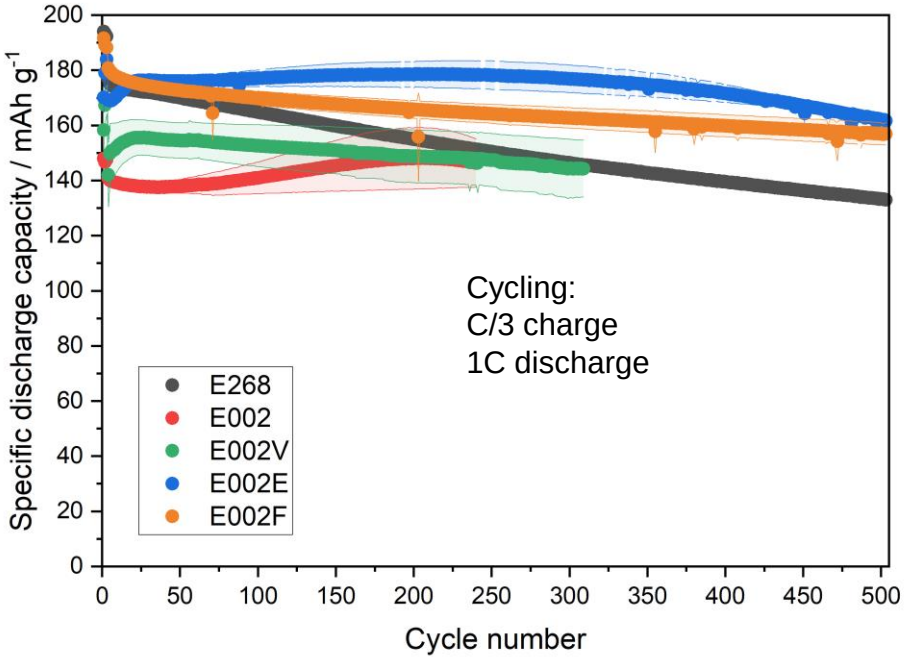
Summary

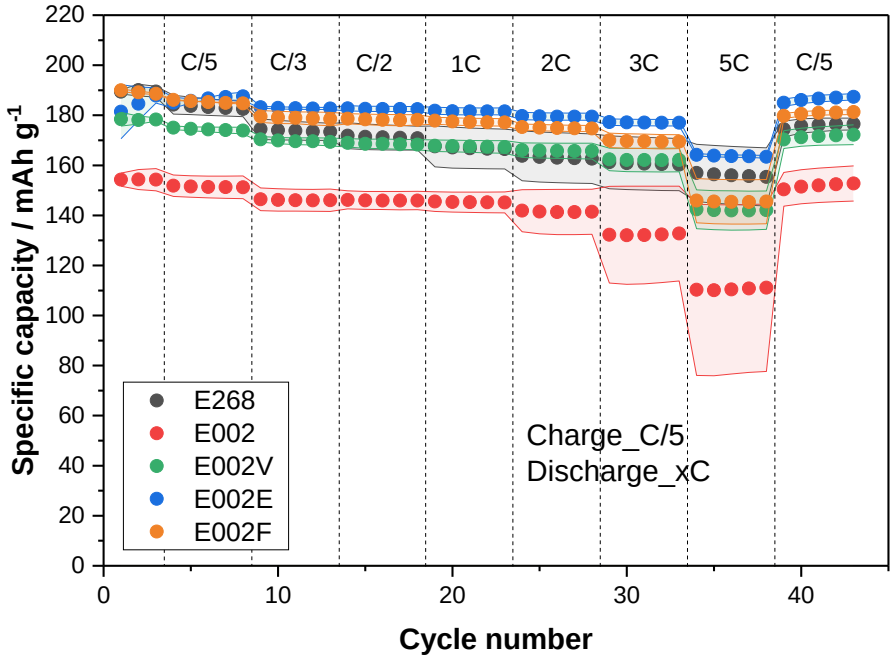
- First-principle calculations in conjunction with diagnostic studies offer predictions of new dopants that stabilizes the $LiNiO_2$ surfaces and bulk lattices.
- We have successfully realized 3D doping and developed MgTi-, MgMn- and Sn-doped Co-free $LNiO_2$ chemistries that meets the energy density target of the project.
- We have developed localized high-concentration electrolytes that introduce a uniform CEI film on the cathode and enhances the stability and cycle life of the MgTi-doped $LNiO_2$ cathode.
- We have scaled up the coprecipitation synthesis with improved hierarchical morphology and tap density control of secondary cathode particles.

Technical Back-Up Divider Slide

Technical Accomplishments and Progress
Optimization of DME-based LHCEs for Gr||NMC811

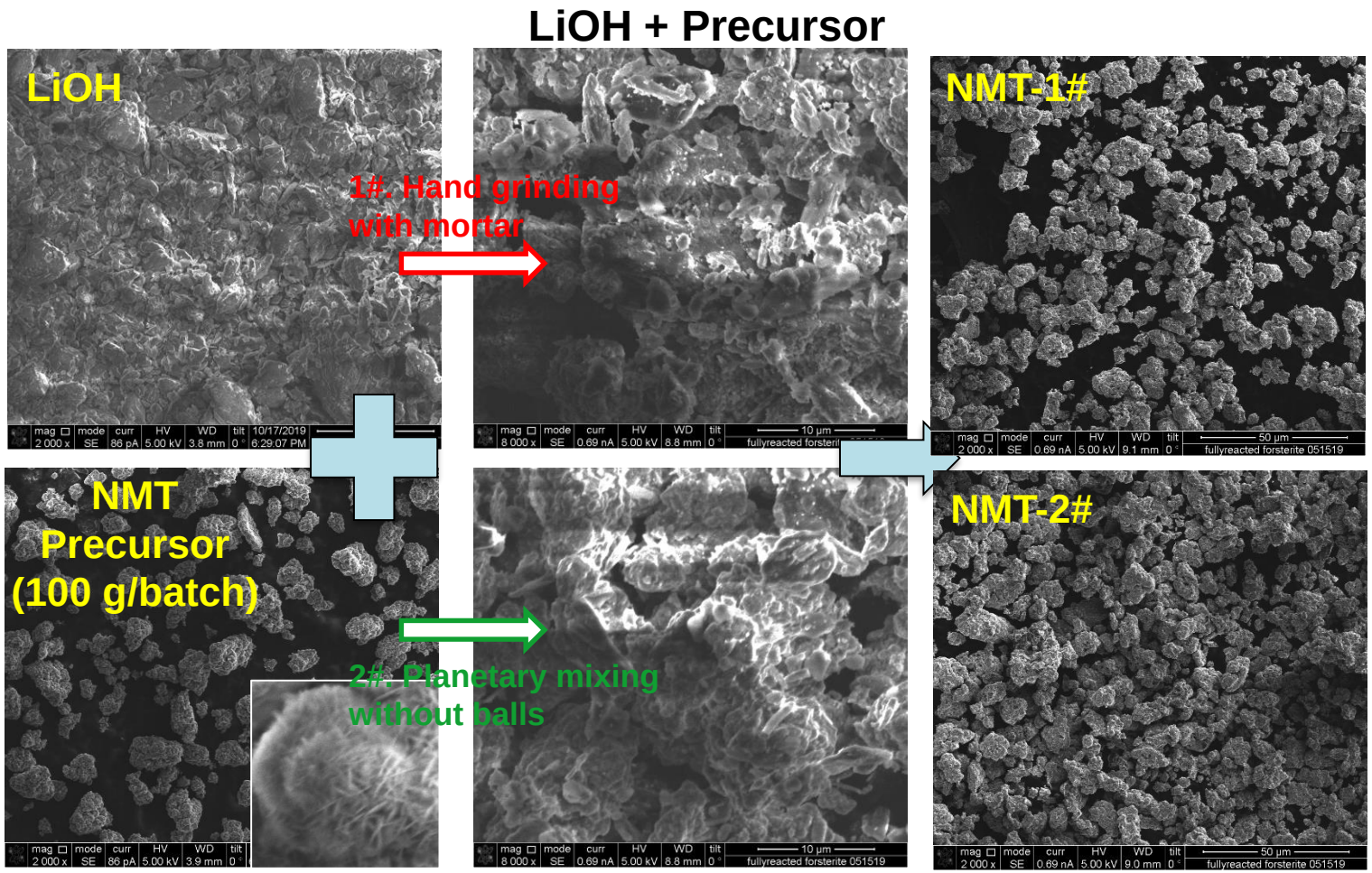
- 4 new DME-based LHCEs (LiFSI in DME-EC/VC/FEC-TTE) were developed for Gr||NMC811 cells.
- NMC811: 1.5 mAh cm^{-2}; Gr: 1.8 mAh cm^{-2} (Both from ANL).
- Voltage range: 2.5 – 4.4 V, 1C= 1.5 mA cm^{-2}. 3 formation cycles: 1×C/20 + 2×C/10.

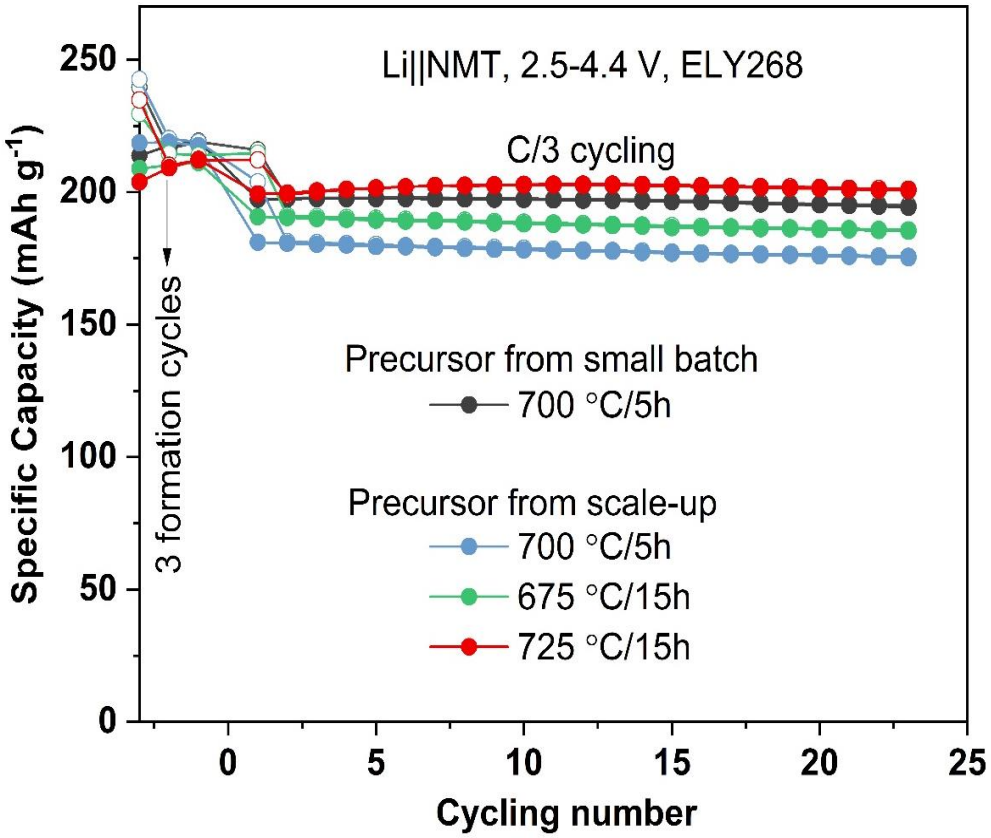




- **Suppressed irreversible capacity in formation cycles by the introduction of EC and FEC into DME-based LHCE.**
- **Superior cycling performance of Gr||NMC811 cells achieved with DME-LHCEs containing EC and FEC.**

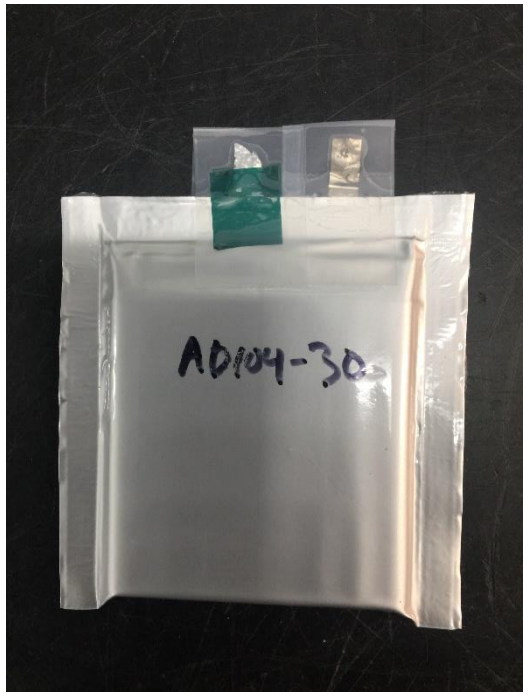
Technical Accomplishments and Progress
Progress on Scaling Up MgTi-doped $LiNiO_2$ (NMT)

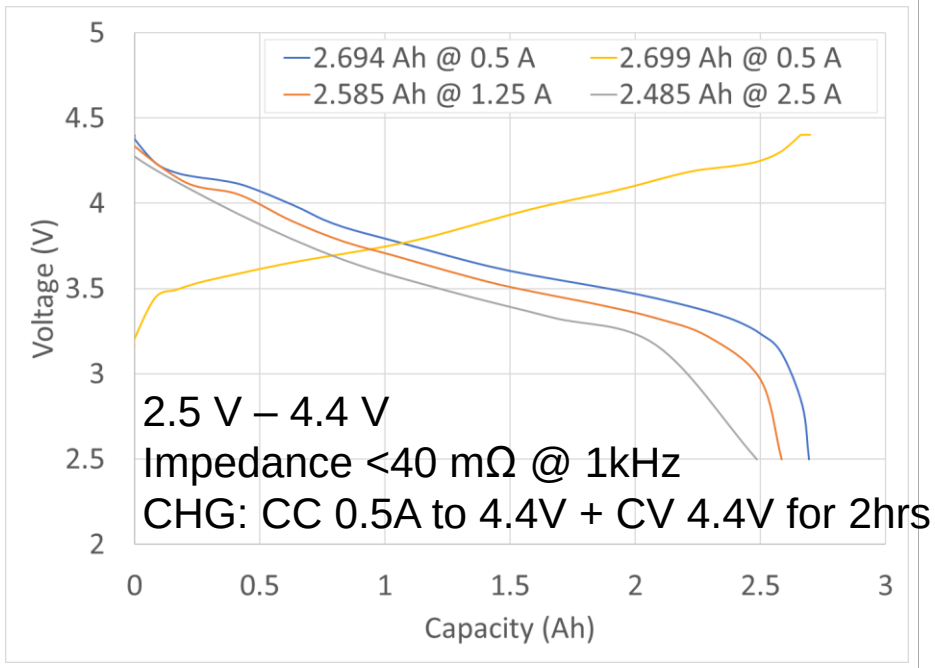


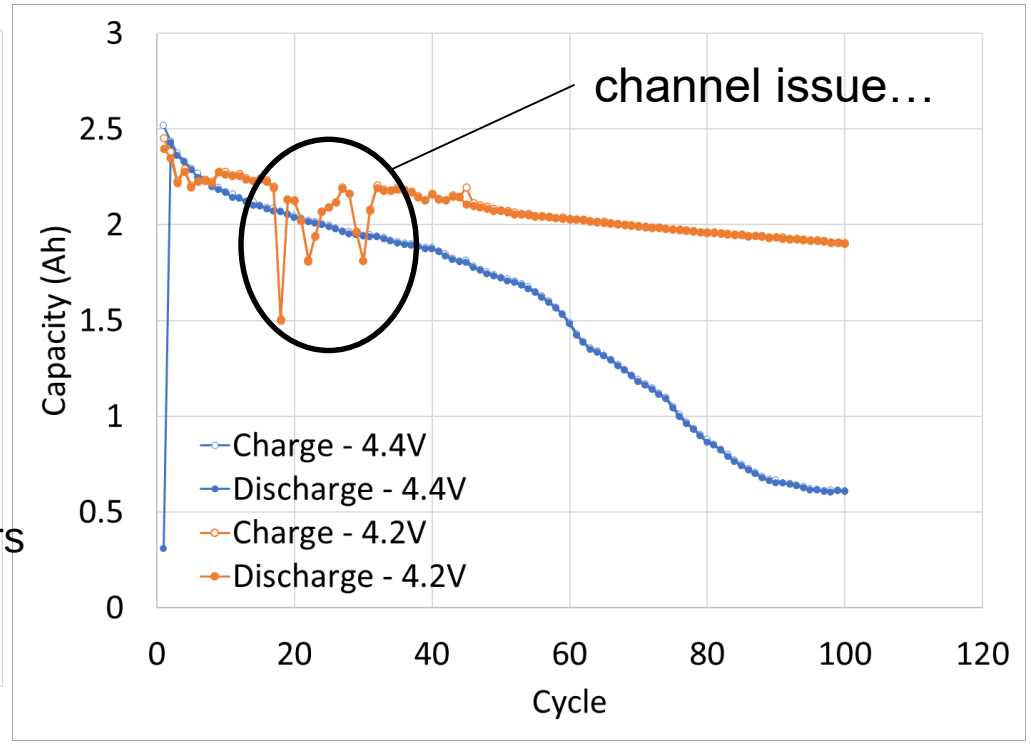


- Hydroxide precursor synthesis has been scaled up to 100 g per batch.
- Optimization of calcination conditions for scaled-up precursor is being conducted.

Technical Accomplishments and Progress
Baseline Project Progress Cell Testing Results







Parameter	Specification
Cathode-level Specific Capacity	219.01 mAh/g
Cathode-level Specific Energy	812.73 Wh/kg
Cell-level Specific Energy	275.60 Wh/kg

Cycling Protocol

- Discharge: CCD to 2.5 V at 0.833 A
- Charge: CCCV to 4.4 V at 0.833 A for 5 hrs